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Synthesis and luminescence properties of $Ca_5(PO_4)_3Cl:Eu^{2+}$ phosphor for solid state lighting

Deorao N. Game[a,*], Nitin B. Ingale[b], Shreeniwas K. Omanwar[a]

[a] *Sant Gadge Baba Amravati University, Camp Area, Near Tapovan Road, Amravati, Maharashtra 444602, India*
[b] *Ram Meghe Institute of Technology and Research, Anjangaon Bari Road, Badnera, Amravati, Maharashtra 444701, India*

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Abstract

A novel method to prepare Eu^{2+} doped chlorapatite phosphor $Ca_5(PO_4)_3Cl$ useful for solid state lighting has been given in this paper. The phosphor was synthesized by the Pechini (citrate gel) method which turned out to be more efficient than the conventional high temperature solid state reaction. The results of the photoluminescence (PL) investigation revealed that it was possible to efficiently excite the phosphor by a UV–visible light from 220 to 430 nm; the phosphor exhibited a bright blue emission at the wavelength $\lambda_{em} = 456$ nm for the excitation wavelength $\lambda_{ex} = 350$ nm of near-ultraviolet light. The developed phosphor emits in blue and, hence, could provide one of the three (RGB) primary color components in a phosphor-converted LED-producing white light.

Keywords: Solid state lighting; Pechini (citrate gel) method; Blue phosphor; Photoluminescence.

1. Introduction

White-light emitting diodes (W-LEDs) are one of the most promising eco-friendly light sources due to their low energy consumption [1]. W-LEDs offer benefits in terms of reliability, energy saving, and safety and therefore have drawn much attention in recent years [2,3]. To increase the efficiency of W-LEDs, special attention has recently been paid to the development of new phosphors with good luminescence properties that can be excited in the long-UV range (300–420 nm). Blue phosphors are an important part in those new phosphors. Recently, W-LEDs have been used in many applications due to the developments in GaN-based chips and phosphor technology. The most popular products in the market are obtained by the combination of a blue-emitting phosphor ($YAG:Ce^{3+}$), which suffer from the low color rendering index (CRI) and high color temperature T_c (usually above 5500 K). These drawbacks can be overcome by the use of triband W-LED, utilizing RGB (red, green and blue) tricolor phosphor coatings on the near ultraviolet (near-UV) LED chip. Blue phosphor $BaMgAl_{10}O_{17}$: Eu^{2+} ($BAM:Eu^{2+}$) has been intensively studied [4,5]. However, $BAM:Eu^{2+}$ has two major drawbacks: thermal degradation and UV damage, which lead to color shift and loss of

* Corresponding author.
E-mail addresses: deorao.game@gmail.com (D.N. Game), cbp.2702@gmail.com (N.B. Ingale), shreeniwasomanwar@gmail.com (S.K. Omanwar).

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brightness [6,7]. Apatite phosphors, which are naturally occurring materials, have recently been used for field-emission displays (FEDs) and would be suitable for white LEDs in the near future because of their low price, environmental friendliness, thermal stability and good photoluminescence properties [8]. Wang et al. [8] reported synthesis of a chloroapatite blue phosphor $(Ca,Mg)_5(PO_4)_3Cl$:Eu with high quantum efficiency using a spray pyrolysis method. The color of the present W-LED depends completely on phosphors because the eyes are not sensitive to the UV output from the W-LED. The market share of the three-band W-LEDs based on near-UV chips has been steadily increasing. Eu^{2+} ions doped alkaline earth halophosphates are efficient blue-emitting phosphors used for triband W-LEDs. The hosts have been paid more attention in many studies because of their high quantum efficiencies and the excellent physical and chemical stabilities [9,10]. At the time they show very interesting physical, and, in particular, optical properties, [11,12]. Several solid solutions of alkaline earth halophosphates like $Ca_5(PO_4)_3Cl$, $Sr_5(PO_4)_3Cl$ and $Ba_5(PO_4)_3Cl$ are known [13]. The substitution of Eu^{2+} for Ca^{2+} is facilitated by the similarity in ionic radii. These phosphors are normally synthesized by solid state reaction which requires very high temperature and it is time consuming also. This prompted us to go for alternative method for the synthesis of such phosphors which would be easy, needs low temperature and less time consuming than solid state reaction.

The present work reports for the first time the synthesis of $Ca_5(PO_4)_3Cl:Eu^{2+}$ phosphor via the Pechini (citrate gel) method and the investigation of its photoluminescent properties.

2. Experimental

For synthesis of Eu^{2+} activated chlorapatite phosphor $Ca_5(PO_4)_3Cl$ stoichiometric amount of the precursors $Ca(NO_3)_2 \cdot 4H_2O$, Eu_2O_3 converted to $Eu(NO_3)_3 \cdot 6H_2O$, $CaCl_2 \cdot 2H_2O$ and $(NH_4)H_2PO_4$ were taken in a china clay basins and dried in a desiccator. All the dried precursors were then finely milled and mixed together. Stoichiometric amount of Citric monohydrated and Ethylene glycol along with 2 drops of Glacial acetic acid were added to dried precursors and stirred continuously.

On slow heating up to 140 °C for ~1 h, the solution boils with the evolution of pale yellowish brown fumes and the process of gelation started. The mixture was then allowed to cool leading to a thick pale yellow gel. The gel was further heated slowly up to 350 °C in air. The polymerization took place and a pale yellow resin/foam was formed and was pyrolysed into stunning black foam at 450 °C, which started burning at 600 °C. The complete pyrolysis took place at 750 °C for 2 h. The white powder so obtained was slowly reduced first at 600 °C for 1 h and then at 970 °C for 3 h in presence of charcoal in order to reduce the trivalent activator to divalent state. Thus white crystalline $Ca_5(PO_4)_3Cl:Eu^{2+}$ phosphor was prepared.

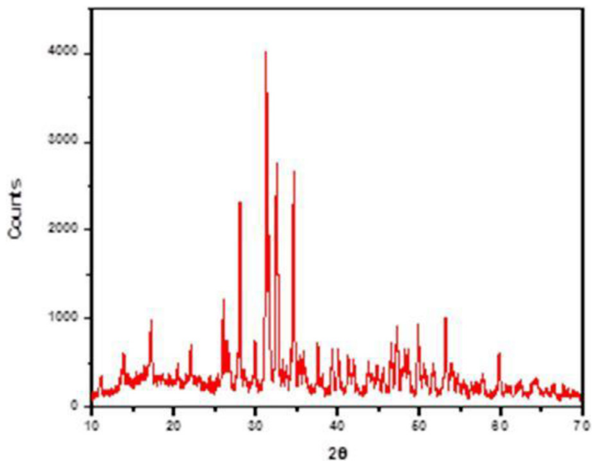

Fig. 1. X-ray diffraction pattern of $Ca_5(PO_4)_3Cl:Eu^{2+}$ phosphor.

3. Results and discussion

3.1. XRD-studies

X-ray diffraction (XRD) pattern of as prepared $Ca_5(PO_4)_3Cl:Eu^{2+}$ phosphor obtained using Rikagu Meniflex II X-ray diffractometer is shown in Fig. 1. The XRD pattern of calcium apatite suggests the formation of a crystalline $Ca_5(PO_4)_3Cl:Eu^{2+}$ matrix. The results of the XRD analysis indicate that almost all diffraction peaks can be indexed to a pure hexagonal $Ca_5(PO_4)_3Cl$ in JCPDS file with file No. JCPDS 33-0271.

3.2. Surface morphology

The phosphor surface morphology was investigated using a Hitachi S-520 scanning electron microscope (SEM). Fig. 2 presents the SEM image of as prepared $Ca_5(PO_4)_3Cl:Eu^{2+}$ phosphor. It can be seen that the particles have some irregular shape and the particle size lies in the range from 5 to 10 μm.

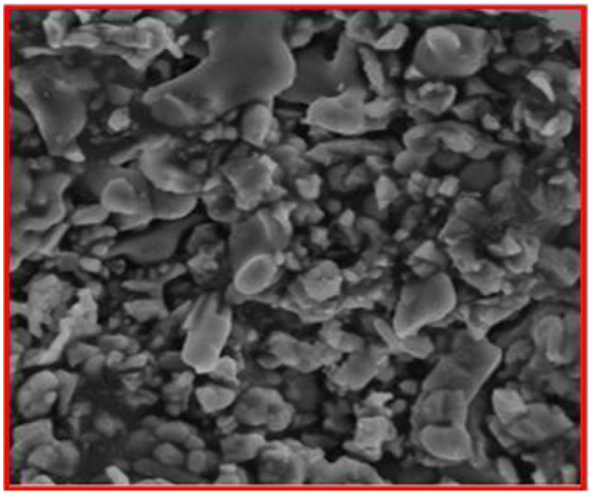

Fig. 2. Scanning electron microscope image of as-prepared $Ca_5(PO_4)_3Cl:Eu^{2+}$ phosphor.

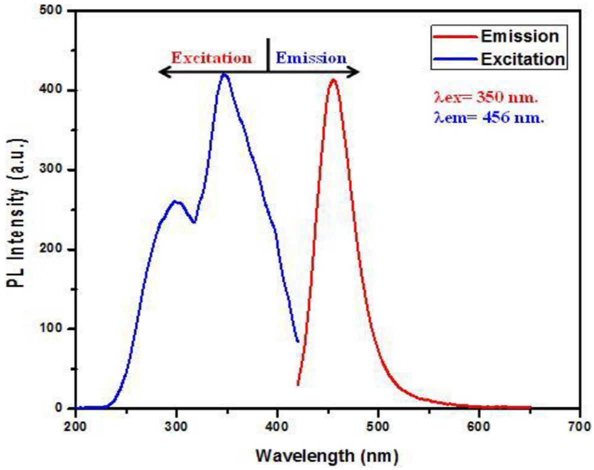

Fig. 3. Photoluminescence emission (*1*) and excitation (*2*) spectra of Eu^{2+} activated $Ca_5(PO_4)_3Cl$ phosphor; $\lambda_{em}=456$ nm, $\lambda_{ex}=350$ nm.

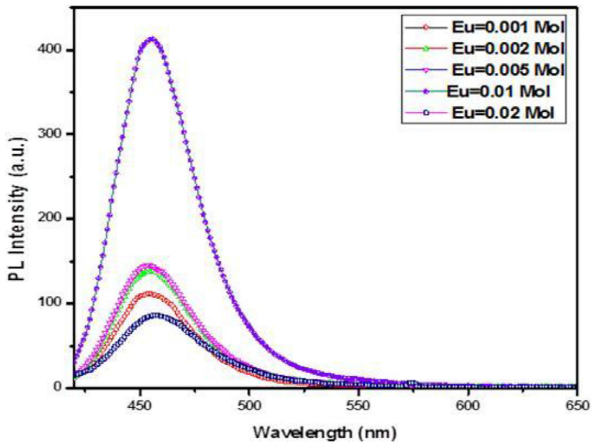

Fig. 4. Photoluminescence emission spectrum of $Ca_5(PO_4)_3Cl$ with different concentration of Eu^{2+}, mol: 0.001 (*1*), 0.002 (*2*), 0.005 (*3*), 0.010 (*4*), 0.020 (*5*).

3.3. Photoluminescence (PL) study

PL measurements were performed at room temperature, using a Hitachi F-7000 Spectrofluorimeter equipped with a 450 W xenon lamp, in the range from 200 to 700 nm, with spectral width of 2.5 nm. Spectra were corrected using Rhodamine B standard by following the procedure prescribed by Hitachi. Prepared phosphors for W-LED meet the basic requirement that exhibits a bright emission under the excitation of near-UV light. Thus, the excitation and emission spectra of the prepared phosphors $Ca_5(PO_4)_3Cl:Eu^{2+}$ were studied in order to assess their potential to be used for near-UV LED based W-LEDs. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra of phosphor prepared are shown in Fig. 3. There are two broad bands in the PLE ($\lambda_{em}=456$ nm) spectra of phosphors, which are due to the transition from $^8S_{7/2}$ $(4f^7)$ ground state of Eu^{2+} to the $4f\,^65d^1$ excited state. The weaker band is located at about 299 nm, and the stronger one is located at around 350 nm with shoulders at 386 nm, which matches well with the emission of commercially available near- UV LED chips. The bright blue emission band with peak at about 456 nm is observed in the PL ($\lambda_{ex}=350$ nm) spectra of this phosphors, which could be attributed to the typical $4f\,^65d^1$ (t_{2g}) – $4f\,^7$ $(^8S_{7/2})$ transition of Eu^{2+} [14].

The concentration of activator has an impact on the performance of a phosphor. Therefore, it is important to determine the composition of the $Ca_5(PO_4)_3Cl:Eu^{2+}$ phosphor with optimal PL emission intensity. A series of $Ca_{5\text{-}x}(PO_4)_3Cl$: xEu^{2+} phosphors with various Eu^{2+} content x was prepared and studied for the effect of activator concentration. The emission spectra of $Ca_5(PO_4)_3Cl:Eu^{2+}$ phosphor ($\lambda_{ex}=350$ nm) with different activator concentration are shown in Fig. 4. No obvious changes were observed for all the samples in our experimental wavelength range, except the fact that the emission intensity of phosphor increases with the increase in Eu^{2+} concentration and reaches the maximum at $x=0.01$ then concentration quenching occurs as the concentration of Eu^{2+} increased above 1%. This type of quenching may be attributed to the fact that energy transfer between two identical ions occurs because the average distance between the activator ions becomes short enough for the energy to migrate and for the killers to reach [15].

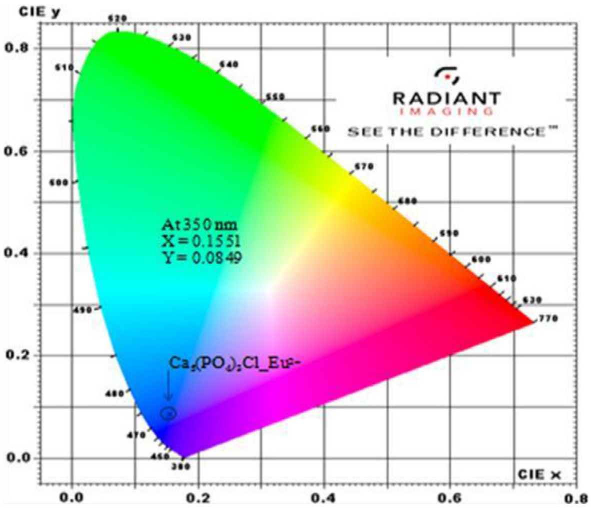

Fig. 5. CIE chromaticity coordinates of $Ca_5(PO_4)_3Cl$: $0.01Eu^{2+}$ phosphor.

3.4. CIE color coordinates

Fig. 5 shows color coordinates CIE (Commission internationale de l'éclairage) 1931 as (0.1551, 0.0849) for $Ca_5(PO_4)_3Cl$: 0.01 Eu^{2+} whereas the commercial blue phosphor $BaMgAl_{10}O_{17}$: Eu^{2+} (BAM:Eu^{2+}) has color coordinates as (0.1417, 0.1072) thus showing better purity of $Ca_5(PO_4)_3Cl$: 0.01 Eu^{2+} as compared to BAM:Eu^{2+} phosphor. Moreover, the color coordinates of the above synthesized phosphor are nearer to those for blue color suggested by the color system EBUPAL/ESCAM, RGBs Blue as well as Adobe blue (0.15, 0.06). Thus the synthesized phosphor is a potential candidate for blue emitting phosphor for solid state lighting using near-UV based W-LEDs.

4. Conclusions

For the first time Eu^{2+} doped chlorapatite phosphor $Ca_5(PO_4)_3Cl$ was synthesized by novel Pechini (citrate gel) method. Photoluminescence measurements showed that Eu^{2+} doped chlorapatite phosphor $Ca_5(PO_4)_3Cl$ synthesized by this method exhibits intensive blue wide-band emission with maximum intensity at 456 nm under near-UV excitation. Both blue and white LEDs can be fabricated by pre-coating the above synthesized phosphors onto 395 nm-emitting InGaN chips. Moreover, the strong absorption of phosphor in the range of 300 nm to 410 nm makes this Eu^{2+}-activated chlorapatite phosphor a potential candidate as a blue component (one of the three primary color components) for fabrication near-UV based phosphor converted white LEDs.

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